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Control of disinfection by-products and biodegradable organic matter through biological treatment
Le contrôle des sous-produits de la désinfection et de la matière organique biodégradable par le traitement biologitlué.

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Résumé de l'article

L'objectif de ce projet, commun à l'Agence Américaine pour la Protection de l'Environnement (USEPA) et l'Université de Cincinnati, est d'optimiser l'usage de la préozonation associée à des procédés biologiques pour le traitement de l'eau de la rivière Ohio en vue de produire une eau biologiquement stable, d'éliminer une partie importante de la demande en chlore, et de réduire le potentiel de formation des sous-produits de la disintection. Ce projet a été conduit à l'échelle pilote et à l'échelle du laboratoire. Pour le traitement biologique, des bioréacteurs, contenant un film biologique sur un sable acclimaté aux eaux de la rivière Ohio, ont été utilisé.

Une attention particulière a été portée à l'étude des sous-produits de la disinfection (DBPs) et de leurs précurseurs.

Les résultats de l'ozonation ont démontré la formation d'aldéhydes : formaidéhyde, méthyl glyoxal, glyoxal et acétaldéhyde. A l'exception du formaldéhyde, les aldéhydes augmentent avec l'augmentation de la dose d'ozone, puis se stabilisent à un rapport d'ozone/carbone organique total (O_3/COT) de 0,7 mg/mg. La formaldéhyde continue à augmenter proportionnellement aux doses d'ozone. Après traitement biologique, la concentration en aldéhydes diminue au dessous de 1 µg/l.

L'augmentation de la dose d'ozone augmente le carbone organique assimilable (COA), (COA P17 ou COA-NOX), ainsi que le carbone organique dissous biodégradable (CODE). Le COA atteint un maximum pour une dose O_3/COT de 2 mg/mg, alors que le COU continue à augmenter avec l'augmentation de la dose d'ozone jusqu'à une dose O_3/COT de 3 mg/mg.

La demande en chlore est réduite par les deux traitements, soit l'ozonation soit les procédés biologiques, respectivement de 75 % par l'ozonation et 55 % par les traitements biologiques.

Des résultats similaires ont été trouvés en ce qui concerne l'effet des différentes doses d'ozone et des traitements biologiques sur les précurseurs des composés organiques halogénés totaux (TOX), les trihalométhanes (THMs) et les acides acétiques halogénés (HAAs). Les précurseurs sont mesurés par le potentiel de formation (FP), (conditions expérimentales : 12 mg/l de chlore, 7 jours de contact, 25 °C et pH 6,5 - 7,2). A une dose d'O_3/COD de 0,4 mg/mg, les TOXFP, les THMFP et les HAAFP sont diminué de 28 %, 23 %, et 33 % respectivement. L'abattement des TOXFP et des THMFP continue légèrement avec une augmentation de la dose d'ozone, alors que les HAAFP sont diminués de façon plus marquée avec une dose d'O_3/COD de 0,87 mglmg. Avec le traitement biologique et même sans préozonation, les TOXFP, les THMFP et les HAAFP diminuent de 39 %, 38 %, et 73 % respectivement. Avec le couplage de l'ozonation et le traitement biologique, les TOXFP et les THMFP sont diminués de 30 à 50 %. Les HAAFP se stabilisent entre 30 et 40 µg/l pour toutes les doses étudiées.

Le potentiel de formation de chloropicrine augmente par l'ozonation mais est réduit de suite par le traitement biologique, jusqu'à moins de 0,2 µg/l.

Donc, pour éliminer les sous-produits de la disinfection, la concentration optimale d'ozone pour l'eau de la rivière Ohio serait entre 0,6 à 1,0 mg/mg (O_3/COT).

En conclusion, l'ozonation diminue la demande en chlore ainsi que les précurseurs des composés organiques halogénés (TOX, THM et HAA). Par contre, l'ozonation produit des autres sous-produits comme les aldéhydes et le chloropicrine et augmente le COA et le COD biodégradable, qui sert par la suite de substrat aux microorganismes. Les procédés biologiques sont efficaces pour diminuer les sous-produits d'oxydation, la demande en chlore et les précurseurs des composés organiques halogénés (TOX, THM et HAA).

Cet abattement permettra l'application de moins de chlore pour maintenir un résiduel dans le réseau et permettra aux usines d'atteindre des normes plus sévères que celles qui sont en effet maintenant.

Control of disinfection by-products and biodegradable organic matter through biological treatment

Le contrôle des sous-produits de la désinfection et de la matière organique biodégradable par le traitement biologique

H.M. SHUKAIRY[1], R.J. MILTNER[2], R.S. SUMMERS[1]

Reçu le 12 novembre 1991, accepté pour publication le 16 juin 1992*.

SUMMARY

The optimal use of ozonation as a pretreatment process prior to biological treatment of Ohio River water was investigated at both the bench (batch) and pilot-plant (continuous flow) scale. The study focused on disinfection by-products (DBPs) and DBP precursor compounds and on the production of biologically stable water. Biotreatment was achieved using a bench-scale fixed-film reactor with sand acclimated to the raw Ohio River water.

Ozonation was found to create a number of aldehydes, in particular formaldehyde, methyl glyoxal, glyoxal and acetaldehyde. With the exception of formaldehyde, a plateau in the aldehyde yield occurred at an ozone to total organic carbon (O_3/TOC) ratio of 0,7 mg/mg, while formaldehyde increased with increasing ozone dose. After biotreatment, the concentration of aldehydes were below 1 µg/l. Increasing ozone doses were also found to increase the assimilable organic carbon (AOC), by both NOX and P17 procedures, and the biodegradable dissolved organic carbon (BDOC). The AOC values showed a maximum at about an O_3/TOC ratio of 2 mg/mg, while the BDOC continued to increase with the highest ozone dose : an O_3/TOC ratio of 2,8 mg/mg.

Both ozonation and biotreatment were found to decrease the chlorine demand by up to 75 % for ozonation and 55 % for biotreatment.

Similar trends were found for the impact of ozonation and biotreatment on the precursor compounds for total organic halogen (TOX), total trihalomethanes (TTHMs) and total haloacetic acids (THAAs), as measured by the formation potential (FP) test : 12 mg/l chlorine, 7 days, 25 °C, 6.5-7.2 pH. An ozone dose of 0.4 O_3/DOC (mg/mg) decreased the TOXFP, TTHMFP and THAAFP by 28 %,

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23 % and 33 %, respectively. Further increases in ozone only marginally increased the amount of the TOXFP and TTHMFP removed, while a maximum removal of 53 % of the THAAFP occurred at O_3/DOC ratio of 0.87 mg/mg. Biotreatment of the nonozonated samples yielded 39 %, 38 % and 73 % removal of the TOXFP, TTHMFP and THAAFP, respectively. Biotreatment of the ozonated sample yielded a 30 to 50 % reduction in TOXFP and TTHMFP, while a constant level of 30 to 40 µg/l of THAAFP was achieved. Chloropicrin formation potential increased with ozone dose, but subsequent biotreatment reduced it to below 0.2 µg/l.

Ozonation was found to oxidize chorine demand and the precursors for TOX, THM and HAAs. However, it created chloropicrin precursors, aldehydes and other biodegradable organic matter. Biotreatment was found to further reduce the chlorine demand, the precursors for TOX, THMs and HAAs and reduce the ozone created disinfection by-products.

Key-words : *river water, ozonation, biodegradation, biodegradable dissolved organic carbon (BDOC), assimilable organic carbon (AOC), aldehydes, disinfection by-products precursors, chlorine demand, TOX, THM, HAA, chloropicrin.*

RÉSUMÉ

L'objectif de ce projet, commun à l'Agence Américaine pour la Protection de l'Environnement (USEPA) et l'Université de Cincinnati, est d'optimiser l'usage de la préozonation associée à des procédés biologiques pour le traitement de l'eau de la rivière Ohio en vue de produire une eau biologiquement stable, d'éliminer une partie importante de la demande en chlore, et de réduire le potentiel de formation des sous-produits de la disinfection. Ce projet a été conduit à l'échelle pilote et à l'échelle du laboratoire. Pour le traitement biologique, des bioréacteurs, contenant un film biologique sur un sable acclimaté aux eaux de la rivière Ohio, ont été utilisé.

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Mots clés : *eau rivière, ozonation, biodégradation, carbone organique dissous biodégradable (CODB), carbone organique assimilable (COA), aldéhydes, précurseurs des sous-produits de la disinfection, demande en chlore, TOX, THM, HAA, chloropicrine.*

INTRODUCTION

Disinfection of drinking water can lead to the formation of disinfection by-products (DBPs) by the reaction of the disinfectant with organic or inorganic matter in the water. Some of these DBPs have been found to be of a health concern. In the early seventies, trihalomethanes (THMs), which result from the chlorination of natural and anthropogenic compounds in water, were found to be potential carcinogens and were regulated by the United States Environmental Protection Agency (USEPA).

In order to minimize DBP formation while still providing adequate disinfection in finished water, modifications in drinking water treatment are necessary. These modifications include the use of alternative disinfectants, as well as more efficient precursor removal.

Microbial regrowth in the distribution system has always been a major concern for the water utilities. The extent of regrowth is dependant on substrate availability and residual disinfection. Biological activity in the treatment plant has been found to reduce the biodegradable organic matter in water. Through such treatment, substrate availability is reduced and the regrowth of pathogenic microorganisms in distribution systems is minimized.

Ozone, a strong oxidant, used most commonly in the US for pretreatment, increases the amount of biodegradable dissolved organic carbon (BDOC) and the rate of biodegradation. Though ozone generates its own DBPs, such as aldehydes and ketones, post-biotreatment is expected to target ozone DBPs, as well as precursors of organic halides.

It is commonly thought that providing a microbially safe water and limiting DBPs are, from an implementation point of view, diamatrically opposed treatment objectives. Biological treatment may in fact economically achieve both objectives.

Objective

The objective of this study was to optimize the use of ozonation as a pretreatment process prior to biological treatment. The study, conducted at both the bench and pilot-plant scale, focused on the removal of DBPs and DBP precursor compounds and on the production of biologically stable water.

The specific water quality parameters of interest were : assimilable organic carbon (AOC), biodegradable dissolved organic carbon (BDOC), total organic carbon (TOC), dissolved organic carbon (DOC), aldehydes, chlorine demand, and the precursor to the DBPs as measured by their formation potential (FP). DBPs measured were trihalomethanes (THMs), haloacetic acids (HAAs), chloropicrin (CP) and total organic halogen (TOX).

The results of this study were used to select an ozone dose for a long term pilot plant study of biological treatment of a surface water.

Disinfection By-product Formation

Although chlorine is a potent disinfectant, it reacts with natural and anthropogenic organic matter in the water to form potentially mutagenic and carcinogenic by-products. Natural organic matter is usually made up of humic and fulvic acids, chlorophyll, proteins, carbohydrates, polysacharides and other components of metabolites of algae and bacteria. The humic material is believed to be the major fraction of the TOC in natural waters (THURMAN, 1985).

THMs, such as chloroform and bromoform, are typically the principle halogenated by-products formed. The total THMs (TTHMs) represent the first group of DBPs to be regulated in the US, by the EPA, at a maximum level of 100 µg/l. Many DBPs formed due to chlorination can be measured by the group parameter total organic halogen (TOX). The sum of the concentrations of the non-THM DBPs (the difference between TOX and TTHMs) were often found to be equal to, or exceeding that of the TTHMs (STEVENS and SYMONS, 1986). Therefore, it is necessary to determine the health impact of this fraction and identify and regulate the appropriate compounds.

The amount of DBP formation is dependent on the natural precursor level in the water, as well as the water source and chlorination conditions.

The presence of bromide during chlorination will affect the composition of the DBPs. Typically, more DBPs are formed and the speciation shifts to the

more brominated products. The rate of bromine substitution is believed to be faster than the chlorine substitution (URANO and TAKEMASA, 1986 ; SYMONS *et al.* 1987). Ozone or chlorine in the water will oxidize low levels of bromide to form hypobromous acid (HOBr), which in turn will initiate addition and substitution reactions.

Investigations of the impact of ozone as a pretreatment, followed by chlorination, have often shown a reduction in THM formation (RECKHOW and SINGER, 1984 ; JACANGELO *et al.* 1989). The extent of reduction was found to depend on the type of the water treated, the organic and inorganic compounds in water, the disinfectant dose, the contact time and the transferred ozone dose (TRUSSELL and UMPHRES, 1978). The DBPs which are formed due to ozonation, such as aldehydes, ketones, carboxylic acids, epoxides and quinones, have not been as widely studied as the THMs. In many of the cases studied, ozonation was found to decrease TOX formation upon subsequent chlorination (RECKHOW and SINGER, 1984 ; JACANGELO *et al.* 1989 ; SHUKAIRY and SUMMERS, 1990).

Another method to reduce DBPs has been the control of precursor material. Studies were directed towards the isolation and identification of the precursors of DBPs in an effort to control and minimize their formation. Better coagulation and filtration techniques have been developed, as well as the use of granular activated carbon to remove the organic precursors (AWWA, 1990).

Biological Treatment

Biologival processes in drinking water treatment have been employed in Europe and to a limited extent in Canada, but not in the US. The removal of color, taste, odor, DBPs and DBP precursors by biotreatment has been reported (JEKEL, 1984 ; HUCK *et al.* 1989). In addition, biodegradation in the filter minimizes substrate availability and prevents regrowth in the distribution system with adequate disinfection.

A number of methods habe been developed to measure the biodegradability of natural organic matter. In general the method either measures the assimilable organic carbon, the biodegradable dissolved organic carbon, or the bacterial growth potential of the water being investigated.

Ozone has been found to enhance the biodegradability of many organic compounds (JANSSENS *et al.* 1984 ; GILBERT, 1987) as it breaks down some of the refractory organics into BDOC (GERVAL and BABLON, 1987). Ozonation of the aromatics in humic substances, at high ozone doses, gives rise to lower molecular weight carboxylic acids that are more easily biodegradable (LANGLAIS *et al.* 1991). Similarly, AOC increases upon ozonation have been reported by many authors (REASONER and RICE, 1989 ; HUCK *et al.* 1989).

The impact of ozone doses on biodegradability has been investigated. For humic substances extracted from Fuhrberg (near Hanover in Germany), the BDOC increased sharply at ozone doses up to 1 mg O_3/mg DOC and continued to increase by only a small amount when the dose was raised to 1.5 mg O_3/mg DOC (WERNER and HAMBSCH, 1986). JAGO and STANFIELD (1984) reported a maximum AOC production at 1 mg O_3/l. Other researchers have

suggested a limit to the ozone dose beyond which no more increase in AOC occurs (BRUNET *et al.* 1982). It seems that beyond a certain dose, all the organic matter that can be converted to a biodegradable fraction are transformed and the rest remain recalcitrant. Studies of the ozonation of aromatic compounds have indicated improvement in biodegradability with high ozone doses due to ring cleavage (GILBERT, 1987).

Therefore, oxidation of the organic matter by ozone increases the substrate availability and if not effectively controlled will contribute to the microbial regrowth in distribution systems and affect water quality (JEKEL, 1984 ; RICE and GOMEZ-TAYLOR, 1989).

MATERIAL AND METHODS

This study utilized raw Ohio River water and was divided into two phases. Phase I of the study investigated the impact of ozone doses on water quality at a pilot scale. Phase II, investigated the impact of ozone doses and subsequent biological treatment on water quality at the bench scale.

In Phase I, ozone was generated with a PCI Model GL-1 which has a 450 g/d capacity. Ozonation was accomplished in a 15 cm diameter counter-current flow-through contactor at a flow rate of 6.4 l/min. Average conditions were : 2.64 m wter depth, theoretical residence time = 7.4 min, T_{10} = 2.27 min, gas/liquid ratio = 0.1 with a transfer efficiency of 94 % or better. This contactor has been described in detail previously (MILTNER *et al.* 1990). In Phase II, ozone was generated with a Sander Ozonizer Model 200 which has a 200 mg/h capacity. Ozone was applied in a batch system with an 87 % transfer efficiency. Applied ozone to the contactor and off-gas from the contactor were measured by UV in Phase I and by iodometry (*Standard Methods*, 1985) in Phase II. Dissolved ozone from the contactor, in both phases, was measured spectrophotometrically using the indigo trisulfonate method (BADER and HOIGNE, 1981).

Samples were collected influent to and effluent from the contactors at both locations and preserved according to the relevant analytic method.

The ozonated sample was divided into two portions, one for biotreatment and the other for formation potential measurement. For BDOC determination, the recirculating bioreactor (MOGREN *et al.* 1990) was used in Phase I. The 500 ml reactors contained 125 ml of sand acclimated with Ohior River water. Vacuum was applied, forcing the incoming air to pass through three humidifier traps. The sample was recirculated at a rate of 30 ml/min, for five days, after which each sample was collected and filtered through a prewashed 0.45 µm (Millipore HV) membrane filter. A modification of the JORET-LEVI (JORET *et al.* 1988) reactor was used for biotreatment in Phase II. The reactor was enlarged to provide enough sample for formation potential tests. A 2l Erlenmeyer flask containing 300 ml of Ohio-River-water-acclimated sand was used, allowing for a sample volume of 1l. Vacuum was applied, forcing the incoming air to pass

through two humidifier traps. At the end of seven days, the samples were taken out of the reactors and filtered through a prewashed 0.45 µm (Millipore HV) membrane filter, prior to formation potential studies and other analyses. Biodegradation was assessed by measuring the difference in DOC before and after biotreatment.

TOC (Phase I) and DOC (Phase II) were measured using EPA Method 415.1.

AOC was measured using the methods of VAN DER KOOIJ *et al.* (1982, 1987). Both the P17 and NOX strains were employed. Growth was expressed as acetate for P17 and as oxalate for NOX. Yield factors and calibration curves were the same as the ones used by VAN DER KOOIJ with a verification of calibration curves.

Aldehydes were measured utilizing the method of SCLIMENTI *et al.* (1990) with the following modifications : thiosulfate was used in the place of ammonium chloride. Rather than use mercuric chloride to prohibit biodegradation between sample collection and derivitization, the samples were derivitized immediatly. Finally, derivitized samples were held for 24 hours at room temperature before extraction.

THMs were measured by EPA Method 551, TOX by EPA Method 450.1, HAAs by EPA Method 552, and chloropicrin by EPA Method 551.

To study formation potentials, the approach described by STEVENS and SYMONS (1977), was used. Samples were chlorinated at 12 mg/l and held headspace-free in the dark at 25° C for seven days at ambient pH (6.5-7.2). Previous studies at EPA had shown that these conditions were typically sufficient to drive the DBP reactions to completion in Ohio River water, resulting in terminal DBP levels. Background, or instantaneous, DBP levels in Ohio River water were not detectable, therefore, DBP formation potentials (DBPFPs) were identical to terminal DBP levels. However, TOXFP results were determined by subtracting the measurable instantaneous results. Chlorine demand was based on the residual chlorine after seven days.

RESULTS AND DISCUSSION

The results of Phase I of the study are shown in figures 1 through 3 and those from Phase II in figures 4 through 8. The error bars in these figures represent duplicate experiments except for figure 2. AOC error bars represent both duplicate experiments and duplicate analyses.

A number of aldehydes were found to increase with ozonation as seen in figure 1. A plateau in the yields of methyl glyoxal, glyoxal and acataldehyde were realized near an O_3/TOC ratio of 0.7. Only the yield of formaldehyde continued to increase significantly beyond that ratio. A number of other compounds were not detected under these ozone conditions : C_3 through C_{10} aldehydes, crotonaldehyde, benzaldehyde, 2-butanone and 2-hexanone.

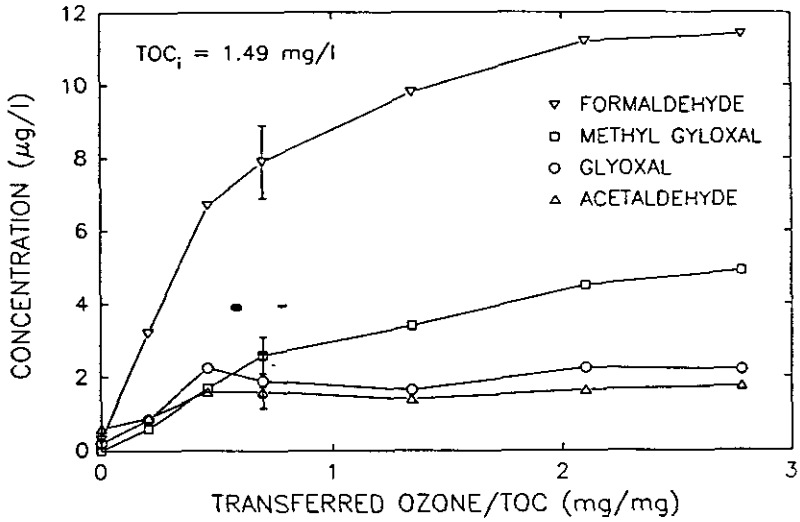

Figure 1 The impact of ozone dose on the formation of aldehydes.
Effets de l'ozone sur la formation des aldéhydes.

As shown previously (LANGLAIS *et al.* 1991), the increase in aldehydes correlates closely with the increase in AOC. This indicates that the aldehydes are substrates for the heterotrophic bacteria utilized in the AOC procedure. Similar to figure 1, figure 2 shows formaldehyde increasing up to an O_3/TOC ratio near 2.0. Similar behavior was noted for both the P17 and NOX strains of AOC. Interestingly, both strains showed decreases in the range of O_3/TOC ratios of 2 to 3. This behavior was not observed at higher ozone doses for BDOC. Figure 2 indicates that BDOC increased with increasing ozone dose in the range tested. It is also interesting to note that on a ug C/l basis, total AOC exceeded BDOC. As noted elsewhere (LANGLAIS *et al.* 1991), AOC is an easily assimilable form of organic carbon and generally its total is less than that of BDOC. The latter measures all forms of organic carbon that can be utilized by bacteria. HUCK (1990) has discussed the significant differences in AOC and BDOC. Both measure biodegradable organic matter, but AOC is based on bacterial enumeration of a certain strain, for a specific substrate and for a certain calibration curve. BDOC is based on organic carbon changes, and as HUCK has noted, comparisons may be troublesome.

As shown in figure 3, oxidation of the precursor for the DBPs, as measured by total THMFP, total HAAFP and TOXFP, did not exceed 20 to 30 % removal, and that level of oxidation was realized before the O_3/TOC ratio reached 0.7. Conversely, chloropicrin formation potential increased four to five times at higher ozone doses, indicating its precursors are of a different nature than the other DBP precursors. HOIGNE and BADER (1988) have discussed the role of nitrogen in chloropicrin's precursor.

If the precursor to major DBPs is decreased by 20 to 30 % by ozonation and the precursor to a minor DBP like chloropicrin is increased by ozonation, then chlorination downstream of ozonation can be critical. Fortunately,

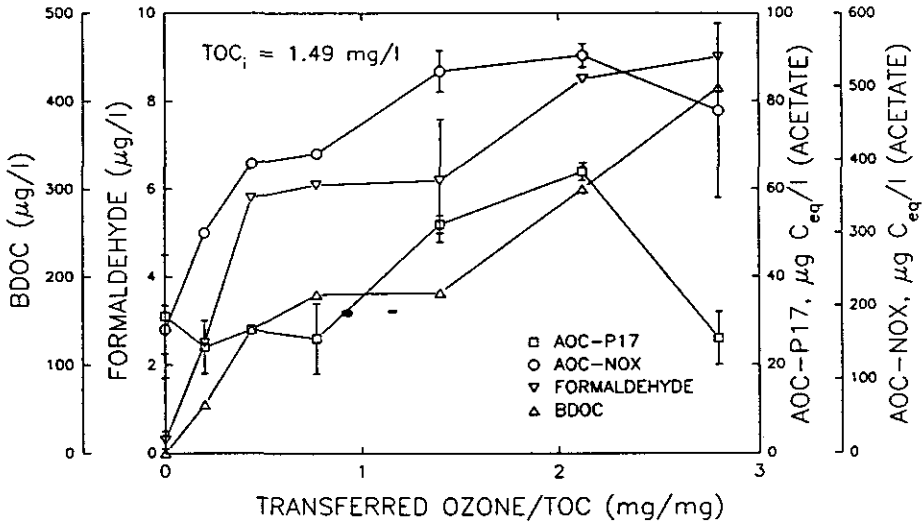

Figure 2 The impact of ozone dose on the formation of formaldehyde, BDOC and AOC.

Effets de l'ozone sur la formation de formaldéhyde, du CODB et du COA.

ozonation can remove about 40 % of chlorine demand at O_3/TOC ratios near 1 and about 60 % at ratios near 2, as shown by these studies *(fig. 3)*. Thus, lower chlorine doses would be required downstream of ozonation, which may result in lower DBP formation.

In Phase II, the impact of ozone doses on biodegradability and on DBP formation was investigated. Figures 4 through 8 show the results of formation potential for some selected DBPs and how these are impacted by ozonation or biodegradation alone, or by a combination of ozone and biodegradation. For the raw and the ozonated water, the percent BDOC was in the range of 1 to 10 %, increasing with the increasing ozone doses. Ozonation has been shown to increase biodegradability (LANGLAIS *et al.* 1991).

The impact of ozone on the formation of the DBPs ; formaldehyde, acetaldehyde, glyoxal and methyl glyoxal is shown in figure 4. Similar trends were observed in Phase I as shown in Figure 1. Higher yields of aldehydes were obtained in Phase II due to a different water matrix and a higher DOC. The DOC in Phase II was about twice that in Phase I. For the four aldehydes shown, the concentration increased with increasing ozone dose. Formaldehyde increased the most, reaching a concentration of 24 µg/l at a transferred ozone dose of 1.64 mg/mg DOC. After biotreatment, a significant reduction in all four aldehydes was observed ; the dialdehydes were reduced to below the detection limit. Formaldehyde and acetaldehyde were reduced by 98 % and 94 %, respectively, after biotreatment, at a transferred ozone dose of 1.64 mg/mg DOC.

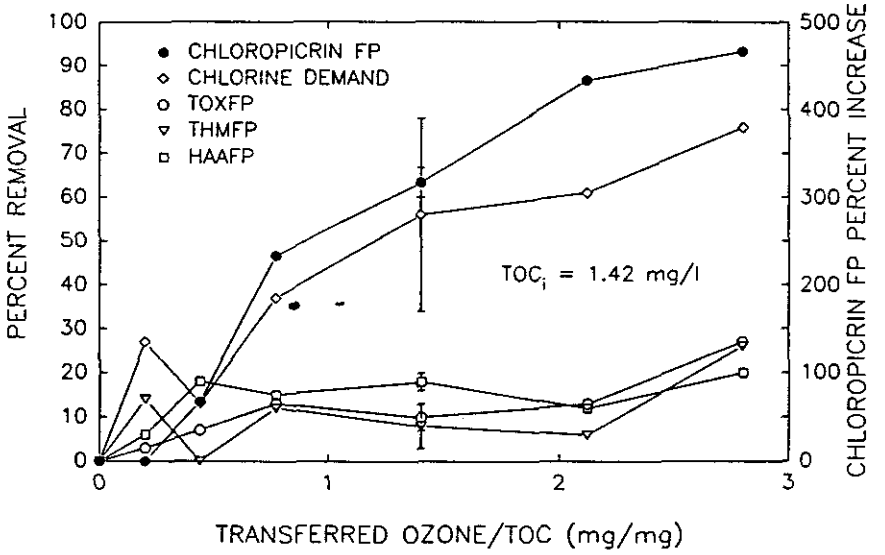

Figure 3 The impact of ozone dose on the control of DBP precursors.
Effets de l'ozone sur le contrôle des sous-produits de la disinfection.

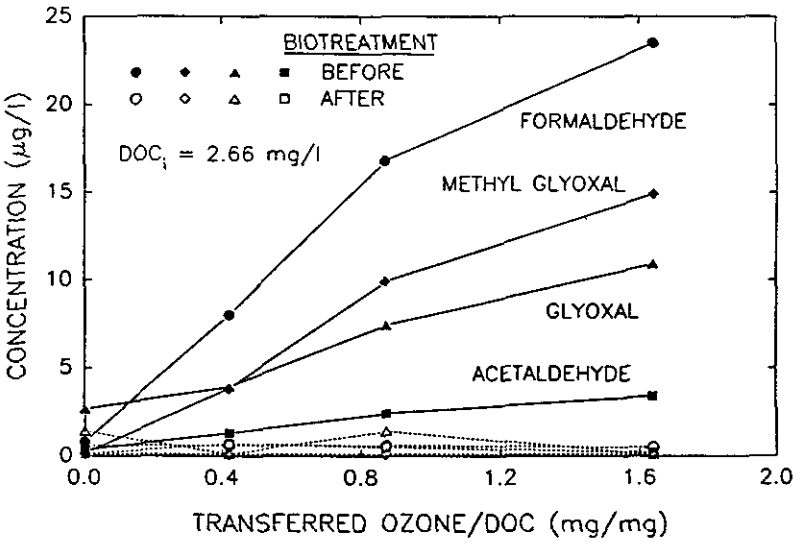

Figure 4 The impact of ozone dose and biotreatment on the control of aldehydes.
Effets de l'ozone et du traitement biologique sur le contrôle des aldéhydes.

As shown in figure 5, the total organic halogen formation potential was reduced by 28 % at a transferred ozone dose of 0.42 mg/mg DOC. At higher ozone doses, the TOXFP was reduced by only a small additional amount. With biotreatment (no ozone applied), TOXFP was reduced by 39 % ; biotreatment

of the preozonated samples caused a further decrease in TOXFP at all ozone doses. A reduction of 30 to 50 % in TOXFP was observed over the range investigated. With or without biotreatment, the impact of ozone dose was more pronounced below a transferred ozone dose of 1 mg/mg DOC. In an earlier study (SHUKAIRY and SUMMERS, 1990), a reduction of 47 % in TOXFP, with preozonation and biofiltration, was observed for Ohio River water at a transferred ozone dose of 2 mg/mg DOC. Ozone alone reduced TOXFP by 17 % in that study ; a chlorine dose of 5 mg/l was used.

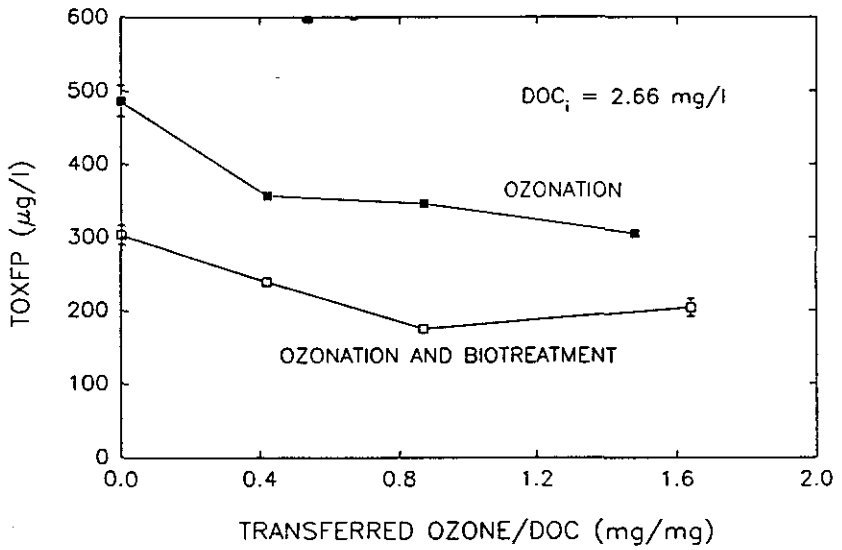

Figure 5 The impact of ozone dose and biotreatment on the control of total organic halogen formation potential.

Effets de l'ozone et du traitement biologique sur le contrôle du potentiel de formation des TOX.

Figure 6 shows the results for TTHMFP. The behavior is similar to that observed for TOXFP. At the lowest ozone dose investigated, TTHMFP was reduced by 23 %, with a slight decrease as the ozone dose increased. The most significant reduction in TTHMFP observed was with biotreatment. About 40 % of the TTHMFP at all ozone doses was removed by biotreatment. The individual THM species formation potential followed different patterns than that observed for the total THMFP. Chloroform FP, which makes up approximately 70 % of the TTHMFP, followed a similar trend as the TTHMFP, at the different ozone doses and upon biotreatment. Dichlorobromomethane FP was not affected by the different ozone doses and was only slightly reduced by biotreatment. The more brominated species displayed a different behavior. Dibromochloromethane FP increased at a transferred ozone dose of 0.42 mg/mg DOC and then gradually decreased. Biotreatment reduced the dibromochloromethane FP to a level similar to that found in the untreated sample. Bromoform FP increased upon ozonation, but remained at the same level at all doses. Biotreatment had no impact on the removal of the precursors of bromoform at any of the ozone doses investigated.

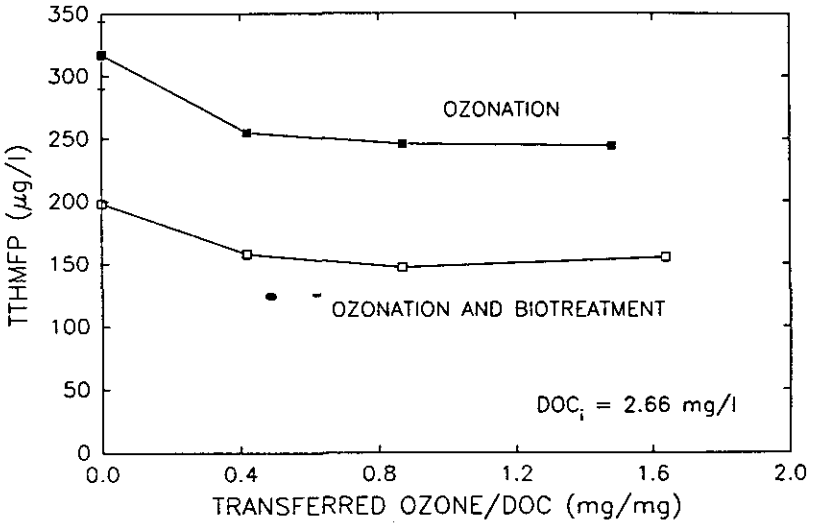

Figure 6 The impact of ozone dose and biotreatment on the control of total trihalomethane formation potential.

Effets de l'ozone et du traitement biologique sur le contrôle du potentiel de formation des TTHM.

The formation potential for the total HAAs was even more impacted by ozonation and biotreatment as shown in figure 7. There seems to be a minimum formation at a transferred ozone dose of 0.87 mg/mg DOC, a reduction of 53 %, after which the concentration increased slightly. Upon biotreatment, the amount of THAAs decreased to a constant level of 30 to 40 µg/l independent of ozone dose, which represented a 75 to 80 % removal of THAAFP. Dichloroacetic acid makes up the largest fraction of the THAAs (50 %), and behaved in a similar manner as the total HAAs. For the dibromoacetic acid however, there was a sharp increase in its formation, at a transferred ozone dose of 0.42 mg/mg DOC, which was reduced upon biotreatment. For the other species, trichloroacetic acid was reduced by 50 % by ozonation alone at all doses, and by 79 % with the combination of the two treatments. Tribromoacetic acid was not detected upon ozonation, but became quantifiable after biotreatment. Ohio River water has a bromide level of approximately 30 µg/l. The combined role of ozone and bromide in increasing the formation potential of the brominated THMs and HAAs has been discussed previously by LANGLAIS *et al.* (1991).

Chloropicrin formation potential results are shown in figure 8. Similar to that found in Phase I *(fig. 3)*, as the ozone dose increased chloropicrin formation increased, up to a factor of three at the highest dose investigated *(fig. 8)*. Upon ozonation, biotreatment significantly reduced the chloropicrin formation potential ; 90 % reduction at the highest ozone dose. For the nonozonated sample biotreatment had little impact.

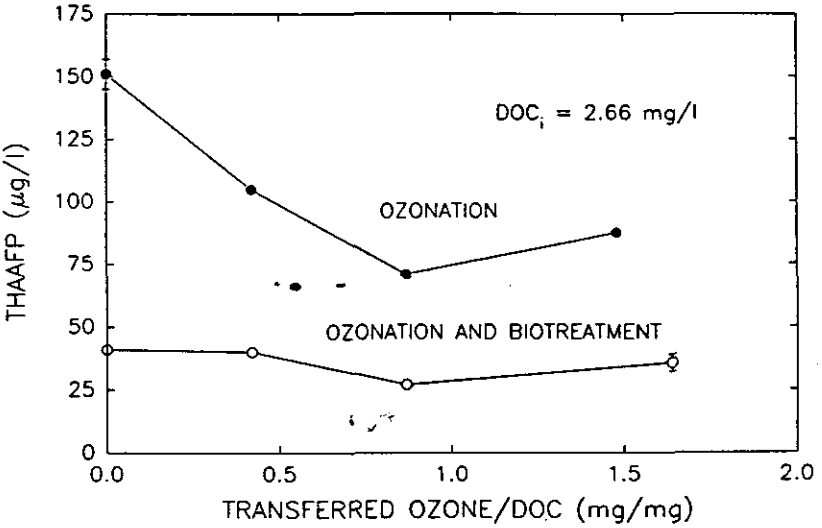

Figure 7 The impact of ozone dose and biotreatment on the control of total haloacetic acid formation potential.

Effets de l'ozone et du traitement biologique sur le contrôle du potentiel de formation des THAAs.

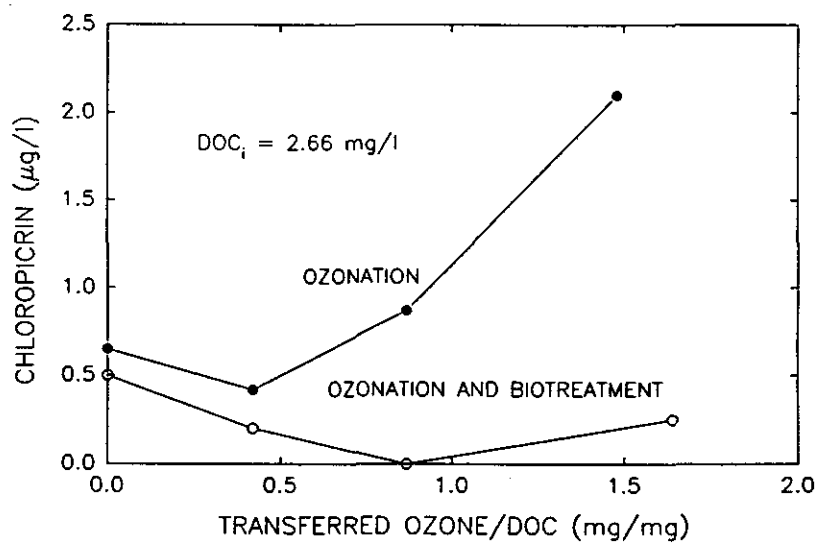

Figure 8 The impact of ozone dose and biotreatment on the control of chloropicrin.

Effets de l'ozone et du traitement biologique sur le contrôle de chloropicrine.

For this phase of the study, preozonation did not seem to have a major impact on the chlorine demand, but biotreatment, at all ozone doses, reduced the demand by 55 %. Ultraviolet absorption, at a wavelength of 254 nm, decreased upon ozonation, by 51 % for the highest dose, with a further reduction by biotreatment of 8 to 18 % for the different reactors.

Similar to Phase I of this study, there seems to be an optimum operational ozone dose range for Ohio River water, from 0.6 to 1.0 mg ozone transferred per mg DOC, to decrease DBP formation potential. All halogenated DBPFPs displayed an initial significant reduction upon ozonation, which leveled off to a plateau as the ozone dose increased. The most reduction in DBP formation potential was with preozonation followed by biotreatment. Preozonation enhanced biodegradability, as measured by BDOC and AOC, but increased chloropicrin formation potential and more significantly increased the aldehyde concentrations. These ozone DBPs were then greatly reduced by biotreatment. This study also indicates the importance of examining the different species of THMs and HAAs, particularly for waters that have a high bromide concentration.

In summary, in addition to preventing regrowth in distribution systems, the combination of ozonation and biotreatment can remove many DBP precursors. All ozone DBPs can be significantly reduced by biofiltration. The chlorine demand is reduced and therefore less chlorine is needed to provide a residual for the distribution system.

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